

# Five Year Integrated M.Sc. Examination, 2017

## Semester - II

### Course: CH-1-2-1

#### ( Chemistry )

Time: Three Hours

Full Marks: 60

Questions are of value as indicated in the margin.

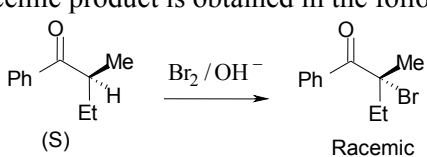
### Group-A

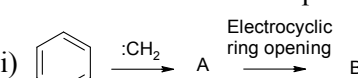
Answer *any two* questions.

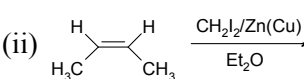
- State Fajans' rules. 2
  - What do you understand by octahedral and tetrahedral holes? Show using figures. 2
  - What are polyhalides? Using VSEPR theory predict the structures of any two type of polyhalides of your choice. 1+2
  - Write a note on non-stoichiometric defect. 3
- What are the different products formed when  $B_2H_6$  is allowed to react with  $NH_3$  at high temperature in 1:1 and 1:2 ratios? Hence establish the structure of the compounds. 2+2
  - Draw the molecular orbital energy level diagram of  $C_2$  molecule. Comment on its magnetic property based on the diagram. 2+1
  - What are extrinsic semiconductors? What are the different types of extrinsic semiconductors? Give examples. 3
- Draw the molecular orbital energy level diagram of HF molecule. 2
  - Write down a method for the synthesis of  $S_4N_4$ . Discuss about its structure and bonding. State one interesting property of the compound. 1+2+1
  - Construct the Born-Haber cycle for the formation of NaCl from Na(s) and  $Cl_2(g)$ . Hence find out the lattice energy of NaCl. Given: Heat of formation of NaCl =  $414 \text{ kJmol}^{-1}$ , Heat of sublimation of Na =  $109 \text{ kJmol}^{-1}$ , Ionisation energy of Na =  $494 \text{ kJmol}^{-1}$ , Bond dissociation energy of  $Cl_2$  =  $121 \text{ kJmol}^{-1}$  and Electron affinity of  $Cl_2$  =  $-347 \text{ kJmol}^{-1}$ . 2+2

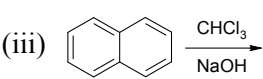
### Group-B

Answer *any two* questions.

- Explain why?
  - Racemic product is obtained in the following reaction 4  


(S)  $\xrightarrow{Br_2/OH^-}$  Racemic
  - $Ph_2CHOH$  is oxidized 6.7 times as rapidly as  $Ph_2CDOH$  using alkaline  $KMnO_4$ . 4
  - The compound cyclohexa-2-4-diene-1-one exists totally in its enol form. 2
- Write notes on: 3x2
    - Secondary kinetic isotope effect
    - Valence tautomerism
    - Non classical carbocations
  - Explain the special stability of the cyclopropyl methyl cations. 4
- Write the structure of the products in the following reactions: 3x2
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i)  $\text{Benzene} \xrightarrow{:CH_2} A \xrightarrow{\text{Electrocyclic ring opening}} B$
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(ii)  $\text{2-methyl-2-butene} \xrightarrow[Et_2O]{CH_2I_2/Zn(Cu)}$
    - 

(iii)  $\text{Naphthalene} \xrightarrow[NaOH]{CHCl_3}$
  - Explain why the addition of singlet carbene to 2-butene is stereospecific whereas, triplet carbene adds in a non-stereospecific manner to the same substrate? 4

P.T.O.

( 2 )

**Group-C**

Answer *any two* questions.

7. a) Show that pressure is a state function for a gas obeying  $(P + \frac{a}{V^2})(V) = RT$ . 2
- b) What are reversible and irreversible processes? Show that the magnitude of the work involved during expansion will be the maximum, if the process is quasi-static or reversible. 1+3
- c) One mole of an ideal gas is heated at constant pressure from 0 °C to 200 °C.
- i) Calculate work done.
- ii) If the gas were expanded isothermally & reversibly at 0 °C from 1 atm to some other pressure  $P_2$ , what must be the final pressure if the maximum work is equal to the work involved in (a). 2+2
8. a) Derive the thermodynamic relationship,  $PV^\gamma = \text{constant}$  for an adiabatic change in volume of an ideal gas, where symbols have their own meaning. 3
- b) Derive the relationship between heat capacities of a gas,  $C_p - C_v = \frac{TV\alpha^2}{\kappa_T}$ , where  $\alpha$  and  $\kappa_T$  are the expansion co-efficient and thermal compressibility factor, respectively. Hence show that the difference between these heat capacities for an ideal gas is equal to 'R', the gas constant. 3+1
- c) 20 g of  $N_2$  at 300 K is compressed reversibly and adiabatically from 20 litres to 10 litres. Calculate the final temperature, q, w,  $\Delta U$ . [Given  $C_v = 5 \text{ cal mol}^{-1}$ ]. 3
9. a) What is the Joule-Thomson's experiment? Show that it is an iso-enthalpic process and hence derive the expression for the Joule Thomson's co-efficient ( $\mu_{JT}$ ) for a van der Waals' gas. 1+3
- b) What are the differences between "Bond Energy" and "Dissociation Energy"? When these two will have the same value? 1+1
- c) Define the term "Heat of neutralization". The heat of neutralization of a strong acid by a strong base is 13.70 kcal, whereas the heat of neutralization of acetic acid by a strong base is 12.60 kcal. Calculate the molar heat of dissociation of acetic acid. 1+3
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